JOURNAL OF CATALYSIS 1, 8–21 (1962)

The Effects of Adsorption of Gases on the Low-Field Magnetization of Nickel-on-Silica Catalysts

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Received September 27, 1961

After a brief account on the magnetic properties of small nickel particles dispersed on a high surface area silica matrix, an experimental setup for the measurement of the influence of the adsorption of gases on the low-field magnetization of nickel-on-silica catalysts is described.

For two catalysts, a coprecipitated nickel-on-silica catalyst and a nickel-on-kieselguhr catalyst, results of these measurements are communicated. For nickel particles behaving superparamagnetically, the decrease in magnetization per adsorbed molecule was the same for hydrogen, carbon monoxide, and oxygen. At high coverages, the decrease by carbon monoxide adsorption was less.

By gradually increasing the mean radius of the nickel particles, an increasing part of them does not behave superparamagnetically.

The effect of adsorption on the magnetization of not completely superparamagnetic systems is twofold. Both an increase, resulting from a lowering of the magnetic anisotropy energy, and a decrease, because the spin pairing of electrons by adsorption decreases the number of unpaired *d*-electrons in the metal, are observed. Possible explanations for the lowering of the magnetic anisotropy are indicated.

INTRODUCTION

The nature of the chemisorption bond of common gases on metal surfaces is still not completely clear. There is, however, empirical evidence (1) that the chemisorption of gases, such as H_2, CO, and N_2, on metals is confined to the transition metals, which are characterized by the presence of empty *d*-levels in the Mott and Jones (2) conception of the structure of metals, or unoccupied atomic *d*-orbitals in the conception of Pauling (3).* From this it may be expected that in systems where a large part of the metal atoms is present in the surface layer, there will be a measurable influence of a chemisorption process on the *d*-electron system of the whole metal. This influence manifests itself in the magnetic properties of the metal. An accurate knowledge of this influence would be very useful for the elucidation of the mechanism of chemisorption.

In measuring the effects of chemisorption of a specified gas, it is necessary to remove the contaminations from the metal surface, for instance by heating *in vacuo* at high temperatures. To prepare a catalyst of sufficient thermostability, the metal can be dispersed on a carrier with a large surface area. The usual preparation techniques (4) mostly yield a system containing isolated metal particles with diameters ranging from 10–500 Å. Since the magnetization of ferromagnetic substances can be easily measured, nickel dispersed on silica makes an interesting object for the study of the influence of adsorption on magnetic properties.

The magnetic behavior of such a system deviates in some respects from that of

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* After atomization hydrogen may also be chemisorbed by *S,P*-metals (5). Culver *et al.* (6) who studied this phenomenon, concluded, however, that it was a bonding type clearly distinct from the bonding on transition metals.

bulk ferromagnetics. Below the Curie temperature the atomic magnetic moments of a ferromagnetic substance are always parallel. The magnetostatic energy of these substances is lowered by the formation of domains so arranged that the magnetostatic energy is minimum.

Ferromagnetic substances can be magnetized in two ways. At a low magnetizing field strength by displacement of the boundary between two domains, or by coherent rotation of the atomic moments of a domain; latter process requires a high field strength. Because both processes require an activation energy, the thermodynamical equilibrium position of the magnetization in the domains and of the arrangement of the domains is generally not attained in a reasonable time with the result that hysteresis is observed. Kittel (7) theoretically explained that below a given particle size (about 150 Å), the energy decrease brought about by the division into domains is smaller than the energy necessary for establishing the domain walls, and, hence, that below this limit the ferromagnetic particles are single domains and can be magnetized only by coherent rotation of their atomic moments. As such a rotation requires a higher activation energy than the displacement of a domain wall, the remanence and the coercive force increase. But as the activation energy needed for rotation is proportional to the volume of the particle, the activation energy decreases again with decreasing particle size until for very small particles the activation energy finally reaches a value of about kT, i.e., the thermal energy. The time necessary for attaining thermodynamic equilibrium is strongly affected by the ratio between the activation energy and the thermal energy, and in a narrow range of particle diameters this time changes from parts of a second into years. So there is a distinct difference between particles that can attain thermodynamic equilibrium in a short time at some temperature and particles that will not do so in a reasonable time. The first kind of particles will not show any remanence. If the energy does not vary with the orientation of the magnetization in the particle (isotropic behavior), such a system of isolated particles will behave just as a system of paramagnetic atoms. The moments of the particles containing 10^2–10^5 atoms are much greater, however, and hence the magnetization at some temperature in a definite field is much greater than for an equal density of paramagnetic atoms. Systems showing this behavior are called "superparamagnetic" (8).

In fact, the magnetic energy for ferromagnetic particles is never isotropic. In the case of randomly orientated particles with uniaxial or cubic anisotropy, there are two extreme cases for which the magnetization can be calculated after establishment of thermodynamic equilibrium (9):

1. When the anisotropy energy is much greater than the orientation energy of the magnetic moments of the particles in the external field, the magnetization is

$$M = M_s(\mu_p H/3kT) \quad (1)$$

if

$$\mu_p H \ll kT$$

where M_s is the saturation magnetization of the system, μ_p is the total magnetic moment of a particle, H is the external field strength, k is the Boltzmann constant, and T is the absolute temperature.

2. When the orientation energy far outweighs the anisotropy energy and $\mu_p H \gg kT$,

$$M = M_s[1 - (kT/\mu_p H)] \quad (2)$$

Whether or not a mathematical expression for the fractional magnetization is available, the only factor determining the fractional magnetization when thermodynamic equilibrium is reached is H/T. Beside the absence of remanence, the superposition of the magnetization data at different field strengths and temperatures as a function of H/T is also a suitable and convenient criterion for superparamagnetic behavior (10).

From experiments on nickel-on-silica catalysts it is known (4) that the nickel particles are present in a range of sizes. If

Eq. (1) describes the magnetization of the particles of a definite dimension, the magnetization for such a system is (11)

$$M = (HI_s^2/3kT) \sum_i n_i v_i^2 \qquad (3)$$

where I_s is the saturation magnetization of nickel at T°K and n_i is the number of nickel particles present with a volume v_i per unit volume of the catalyst.

The saturation magnetization of the catalyst is

$$M_s = I_s \sum_i n_i v_i \qquad (4)$$

hence, the fractional magnetization is

$$\frac{M}{M_s} = \frac{HI_s}{3kT} \frac{\sum n_i v_i^2}{\sum n_i v_i} = \frac{HI_s}{3kT} \frac{\overline{v^2}}{\bar{v}} \qquad (5)$$

Thus if the saturation magnetization of the system is known, the value of $\overline{v^2}/\bar{v}$ can be calculated from the slope of the tangent to the M/M_s versus H/T curve in the origin.

Because of the thermal disordering, the field strength necessary for saturating the nickel particles is much higher than that for bulk ferromagnetics. Owing to this, saturation of the smallest nickel particles present in a nickel-on-silica catalyst can only be satisfactorily approximated from measurements at liquid helium temperature and high field strengths (about 10 koe). Investigation of the effect of adsorption on the saturation magnetization at higher temperatures requires so high a field strength as can only be maintained for very short times (12). The magnetization at low field strengths can be measured much more easily and, for that reason and also for measuring the effect at higher temperatures, investigation of the behavior of the low-field-strength magnetization on adsorption is very attractive.

The first experiments of this kind were performed by Selwood (13). On adsorption of hydrogen on a nickel-on-silica catalyst, he usually observed a decrease in magnetization; only at low temperatures an occasional increase was found (14). Beside these low-field experiments, Selwood and Dietz (15) investigated the behavior of the saturation magnetization on hydrogen adsorption. Only at 4.2°K and field strengths of about 10 koe could they satisfactorily approximate saturation. In these measurements a decrease in saturation magnetization was always observed.

Just like this decrease, the decrease in low-field magnetization can be very easily explained by the pairing of unpaired *d*-electrons of the nickel with the valence electrons of the chemisorbed hydrogen atoms or by the destruction of the ferromagnetic behavior of the nickel surface atoms to which the adsorbed atoms or molecules are attached. The increase, however, could not be explained in a simple manner. Because of the aforementioned importance of magnetization measurements at low field strengths, we started an investigation to explain the fact that one and the same gas can increase the low-field magnetization and decrease the saturation magnetization on adsorption.

EXPERIMENTAL PROCEDURE

(*a*) *Measurements of the Magnetization*

For measuring the magnetization an apparatus was developed analogous to the "permeameter" of Selwood (13), see Figs. 1 and 2. Two pick-up coils were inserted into two equal water-cooled air coils capable of providing a root-mean-square field strength of about 450 oe. The wires (0.2 mm platinum) of the pick-up coils were directly wound on asbestos-covered cylindrical Pyrex vessels (63 turns, height 45 mm, diameter 22 mm). The resistance of each coil was 17 ohms. The primary coils (914 turns of 2-mm copper wire) were 125 mm high, with an external diameter of 210 mm and an internal diameter of 70 mm. They were fed with a stabilized current of variable strength and a frequency of 50 cycles/sec.

One of the pick-up coils contained the sample, the other was empty. The voltage difference across the two coils was measured with a Philips ac electronic voltmeter (type GM 6012). To cancel the signals from the two coils, when both are empty, either coil was connected to a 1-meg resistor—such a high resistance being necessary to keep the phase difference negligible—and a variable part of the voltage difference across a 1-meg resistor could be taken (Fig. 2). By carefully shielding all leads, the sensitivity for stray signals was reduced so far that the measured voltage difference was constant within 0.02 mv.

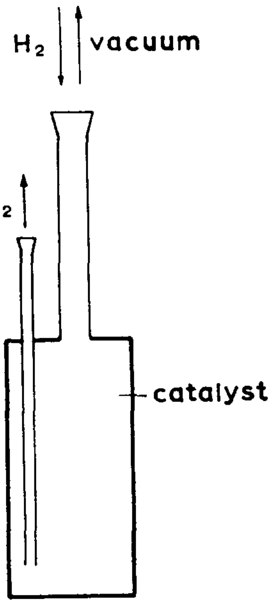


FIG. 1. Measuring cell.

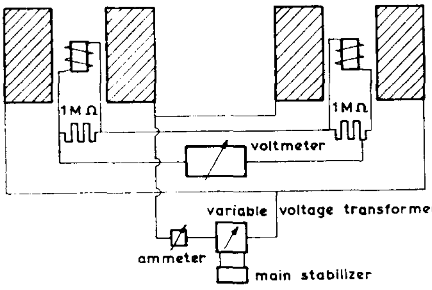


FIG. 2. Electrical system.

Using a small sleeve heater (NiCr wire wound around a glass cylinder), the sample could be heated inside the primary coil; a Dewar vessel was installed for measurements at low temperatures. To ensure good thermal contact, the measurements were performed at a He pressure of 0.3 mm Hg.

(b) *Preparation of the Catalysts*

Two types of catalyst were examined—a coprecipitated nickel-on-silica catalyst and an impregnated nickel-on-kieselguhr catalyst. The coprecipitated catalyst was prepared by quickly mixing boiling solutions of potassium metasilicate and nickel nitrate. The precipitate was washed with distilled water, filtered off, and dried at 110°C for 16 hr. The nickel content was 41½%.

The impregnated nickel-on-kieselguhr catalyst was prepared by grinding (in a ball mill) nickel nitrate, water, and kieselguhr previously washed with nitric acid. During the grinding, ammonium nitrate was slowly added. The catalyst was filtered off, washed with distilled water, and dried at 110°C for 16 hr. The nickel content of this catalyst was 15.8%. The catalysts were reduced *in situ* in flowing hydrogen, which was purified via a Deoxo catalyst and a cold trap. After reduction, the sample was heated *in vacuo* to a final pressure of 10^{-6} mm Hg. The pumping device was a mercury diffusion pump backed by a rotary oil pump. When the hot catalyst was disconnected from the pumps, the pressure did not rise above 10^{-4} mm Hg in 2 hr.

Hydrogen used in the adsorption experiments was purified by diffusion through palladium; carbon monoxide was obtained by decomposition of formic acid, and oxygen was taken from a cylinder. The amounts adsorbed were measured with a U-tube Hg manometer or a McLeod manometer.

RESULTS

In Fig. 3 the magnetization, after correction for the change in saturation magnetization of bulk nickel with temperature, is plotted versus H/T for the coprecipitated nickel-on-silica catalyst. Correction was effected by multiplication by $I_{s_0}^2/I_{s_T}^2$, where I_{s_0} is the saturation magnetization at 0°K and I_{s_T} is the saturation magnetization at T°K. The values were taken from a paper by Weiss and Forrer (16). The catalyst was reduced at 360°C for 59½ hr. After evacuation and measuring the hydrogen adsorption effect at a cer-

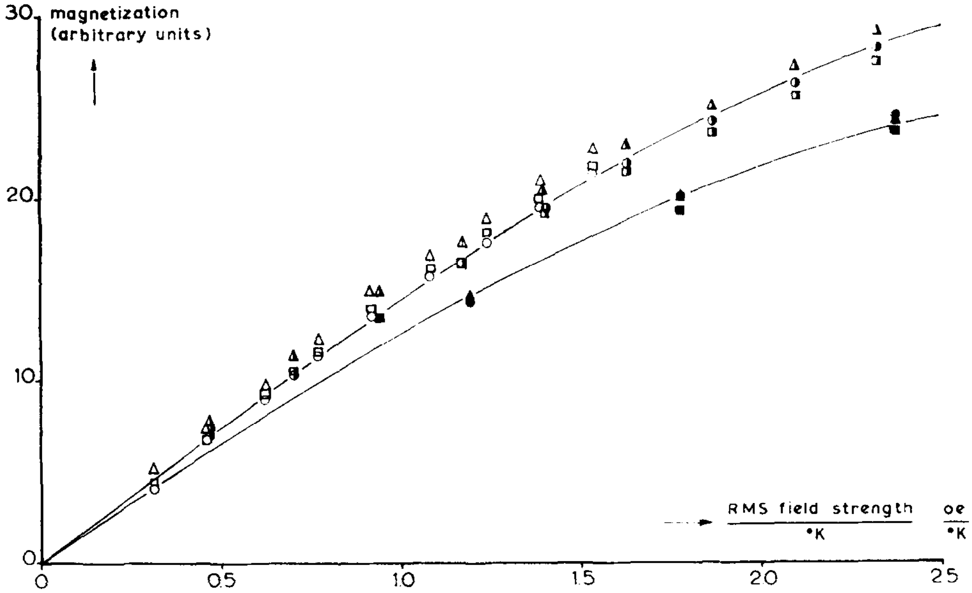


FIG. 3. Dependence of the magnetization of the coprecipitated nickel-on-silica catalyst on field strength and measuring temperature. Catalyst, 59½ hr reduced at 360°C. KEY: (□) After 183 hr evacuation at 360°C; (△) after 222 hr evacuation at 360°C; (○) after 255 hr evacuation at 360°C; (□ △ ○) measured at 296°K; (◨ ▲ ◑) measured at 196°K; (■ ▲ ●) measured at 77°K.

tain temperature, the catalyst was heated *in vacuo* at 360°C and the hydrogen adsorption was measured at another temperature. To be sure that during heating no additional sintering occurred, the magnetization after reevacuation was determined again at various field strengths and at different temperatures. The total pumping times are indicated in the caption of Fig. 3. After 183 hr. of evacuation at 360°C, prolonged pumping appeared to bring about no sintering as the curves did not change beyond the measuring reproducibility. Beyond 196°K, the nickel particles are superparamagnetic, as can be concluded from the superposition of the data measured at 196° and 296°K. At 77°K, the sample is not superparamagnetic.

As we cannot determine saturation magnetization experimentally, M_s was calculated by means of an empirical extrapolation method outlined by Heukelom *et al.* (17), and from the slope of the M/M_s versus H/T curve, in the origin $\overline{v^2}/\overline{v}$ appeared to be 3.36×10^{-20} cm³, corresponding to a "mean radius" of 20 Å.

Figure 4 represents the influence of hydrogen adsorption on the magnetization of the catalyst measured at three temperatures and a field strength of 320 oe. Upon admission of hydrogen to the catalyst, the same extra decrease in magnetization, owing to the liberation of the heat of adsorption as was reported by Selwood (14), is observed. Within a few minutes this extra decrease disappeared. The values indicated in Fig. 4 were measured after the voltage difference had become constant within 0.02 mv. When the catalyst temperature was 77°K, only about 2 cm³/g nickel were adsorbed instantaneously; after that the adsorption proceeded slowly. The change in magnetization showed the same behavior. The adsorption was completed by warming up the catalyst to room temperature and cooling it down again to 77°K. The occurrence both of instantaneous and of slow adsorption was also observed with nickel-on-silica catalysts by Schuit and de Boer (18) and, with evaporated nickel films, by Beeck *et al.* (19), by Gundry and Tompkins (20), and by Knor and Ponèc (21).

In the temperature range where the

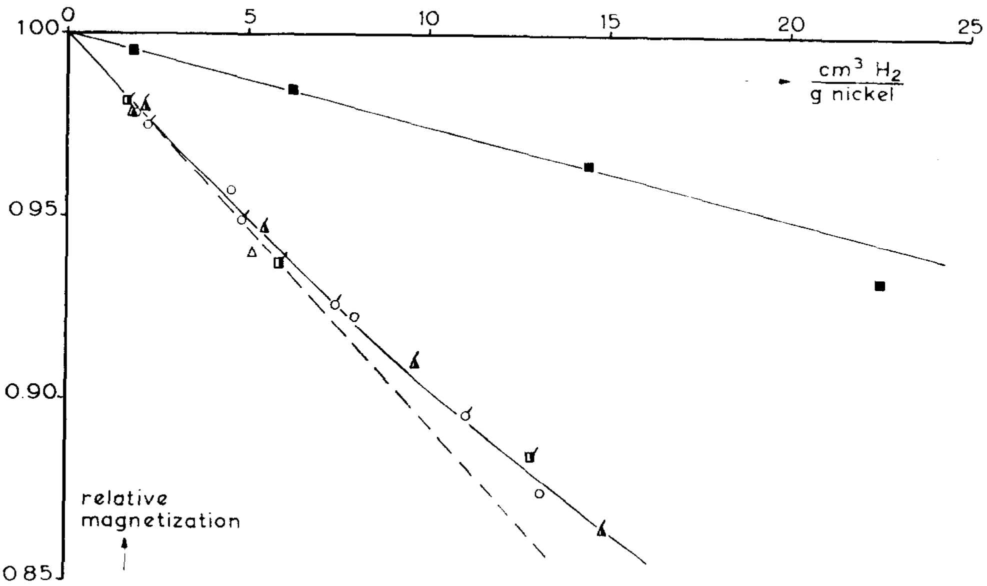


FIG. 4. Effect of hydrogen adsorption on the magnetization of the coprecipitated nickel-on-silica catalyst. Catalyst, 59½ hr reduced at 360°C. KEY: (■) Measured at 77°K after 183 hr evacuation at 360°C; (◨) measured at 196°K after 202½ hr evacuation at 360°C; (△) measured at 296°K after 222 hr evacuation at 360°C; (◭) measured at 196°K after 239 hr evacuation at 360°C; (○) measured at 296°K after 255 hr evacuation at 360°C; (◔) measured at 296°K after 272 hr evacuation at 360°C.

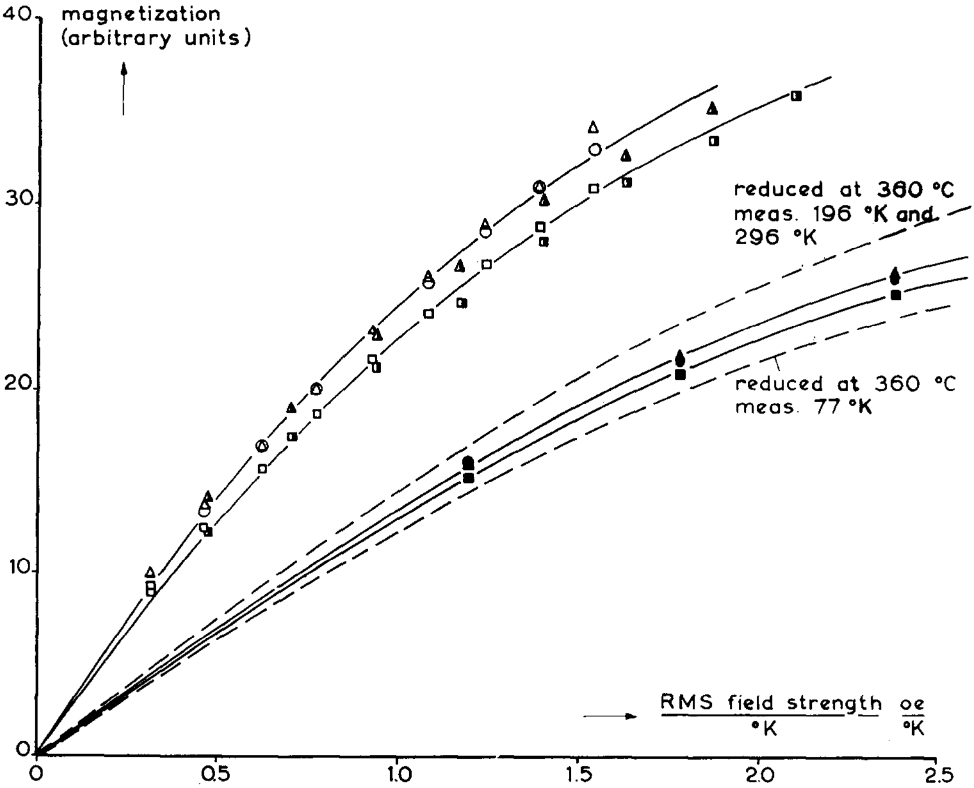


FIG. 5. Dependence of the magnetization of the coprecipitated nickel-on-silica catalyst on field strength and measuring temperature. Catalyst, 26 hr reduced at 525°C. KEY: (□) After 40 hr evacuation at 525°C; (△) after 64½ hr evacuation at 360°C; (○) after 101 hr evacuation at 360°C; (□ △ ○) measured at 296°K; (◨ ◭ ◑) measured at 196°K; (■ ▲ ●) measured at 77°K.

nickel particles behave superparamagnetically, the effect of hydrogen adsorption does not depend on the measuring temperature, as can be concluded from the superposition of the data measured at 196° and 296°K. The effect of hydrogen adsorption on the magnetization measured at 77°K is appreciably lower.

From Fig. 5 it appears that after reduction of the catalyst at 525°C and heating *in vacuo* at the same temperature, the mean diameter of the nickel particles had increased. Heating *in vacuo* for 64½ hr at 360°C caused some additional sintering. At 196°K, superparamagnetic behavior is still present, but at 77°K the deviation from it is larger than was observed on a catalyst reduced at 360°C. For $\overline{v^2}/\bar{v}$, a value substantially greater than that found in the latter case was calculated, viz., 20.5×10^{-20} cm³, which corresponds to a mean particle radius of 36 Å. Figure 6 represents the effect of hydrogen adsorption. Now the magnetization measured at 77°K increased on hydrogen adsorption; measurements at 90°K showed a slightly smaller increase.

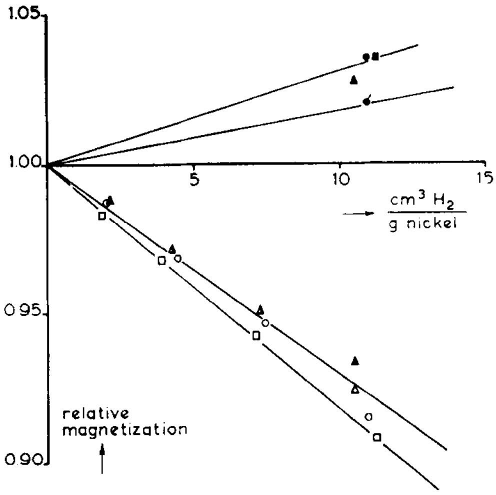


FIG. 6. Effect of hydrogen adsorption on the magnetization of the coprecipitated nickel-on-silica catalyst. Catalyst, 26 hr reduced at 525°C. KEY: (□) After 40 hr evacuation at 525°C; (△) after 64½ hr extra evacuation at 360°C; (○) after 101 hr extra evacuation at 360°C; (□ △ ○) measured at 296°K; (▲) measured at 196°K; (◐) measured at 90°K; (■ ▲ ●) measured at 77°K.

The fact that the decrease is independent of the measuring temperature in the superparamagnetic temperature region is demonstrated again by measurements at 196° and 296°K, but the slope of the curves found for systems with a different mean particle radius varies, as can be concluded from a comparison of the experimental data at high temperatures in Figs. 4 and 6. When the mean particle radius increases, the influence of hydrogen adsorption diminishes.

In Fig. 7 the influences of hydrogen and carbon monoxide adsorption on magnetization are compared for the catalyst reduced at 360°C; the same is done for hydrogen and oxygen adsorption on the catalyst reduced at 525°C. To prevent additional sintering by the heat of adsorption of oxygen, the gas was admitted slowly at 77°K. The effects of hydrogen, carbon monoxide, and oxygen adsorption on the magnetization of superparamagnetic nickel particles were equal, as appears from the experimental data.

Outside the superparamagnetic temperature range, however, the influences of hydrogen and oxygen adsorption differ. Oxygen adsorption causes the magnetization at 77°K to decrease slightly, whereas hydrogen shows the reverse effect, the same was observed by Leak and Selwood (22) working with a sintered nickel-on-kieselguhr catalyst at 196°K. In Fig. 8 magnetization measurements are plotted for a nickel-on-kieselguhr catalyst after reduction for 111½ hr and heating *in vacuo* for 21 hr at 205°C; the $\overline{v^2}/\bar{v}$ amounted to 34×10^{-20} cm³, from which a mean particle radius of 43 Å can be calculated. When the catalyst was heated again *in vacuo* at 205°C for 109 hr after hydrogen adsorption, the magnetization versus H/T plot revealed additional sintering; $\overline{v^2}/\bar{v}$ was 38.6×10^{-20} cm³ and the mean particle radius, 45 Å. Already at 196°K the sample was no longer superparamagnetic, the points measured at 196°K not being situated on the 296°K line. After sintering for 41 hr at 310°C *in vacuo*, prolonged pumping at 210°C did not effect further sintering (Fig. 9); the $\overline{v^2}/\bar{v}$ amounted to 79×10^{-20} cm³ and the mean particle radius to 57 Å. The decrease in the magnetization of these nickel particles, measured at 296°K on hydrogen adsorption, is lower than for the nickel particles present prior to sintering at 310°C (Fig. 10). Hydrogen adsorption increased the magnetization measured at 196°K, and the increase in magnetization measured at 77°K is still larger. In each of these cases the magnetization reached a maximum after which it decreased again. After sintering at 490°C for 16½ hr, the deviation from superparamagnetic behavior is still larger (Fig. 11). In this case the nickel particles do not behave superparamagnetically at the highest measuring temperature (296°K). Hence, part of the nickel particles is not measured and the mean particle dimension could not be calculated. Now the adsorption of hydrogen increased also the magnetization measured at 296°K (Fig. 12).

On hydrogen adsorption, the magnetizations measured at 77° and 196°K showed the same pattern as prior to sintering at 490°C. However, the maxima of the magnetizations were higher than for the catalyst sintered at 310°C. Oxygen adsorbed on the catalyst sintered at 490°C caused a small increase in magnetization at 77°K and a small decrease in magnetization at 296°K.

All results presented here appeared to be well reproducible. Some additional measurements were performed on commercial nickel-on-carrier catalysts; in these meas-

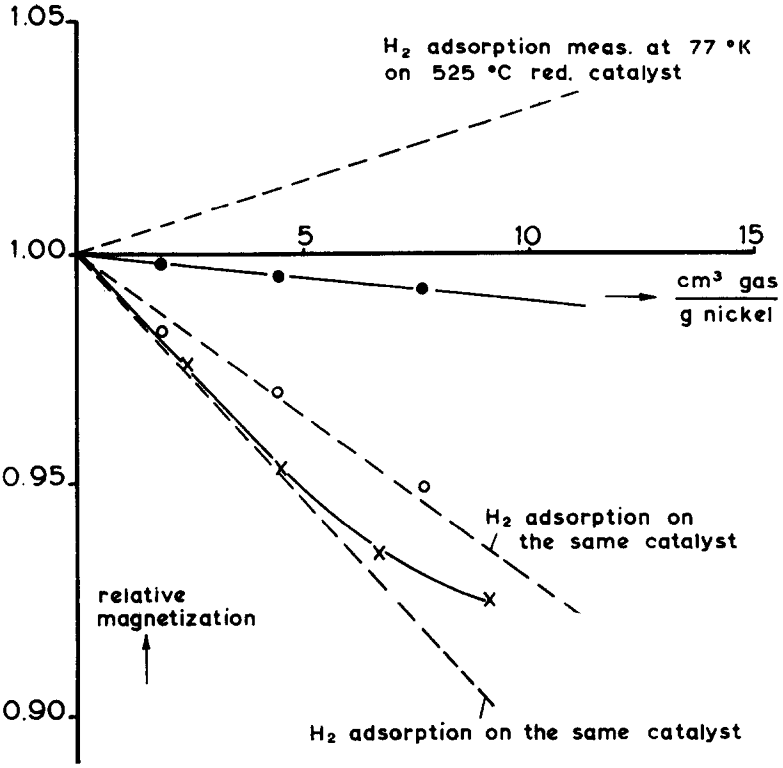


FIG. 7. Comparison of the effects of carbon monoxide and hydrogen adsorption and of oxygen and hydrogen adsorption on the magnetization of the coprecipitated nickel-on-silica catalyst. KEY: (×) Carbon monoxide adsorption; catalyst, 59½ hr reduced at 360°C and 316½ hr evacuated at 360°C, measured at 296°K; (○ ●) Oxygen adsorption; catalyst, 26 hr reduced at 525°C; 40 hr evacuated at 525°C and 122 hr at 360°C; (○) measured at 296°K; (●) measured at 77°K.

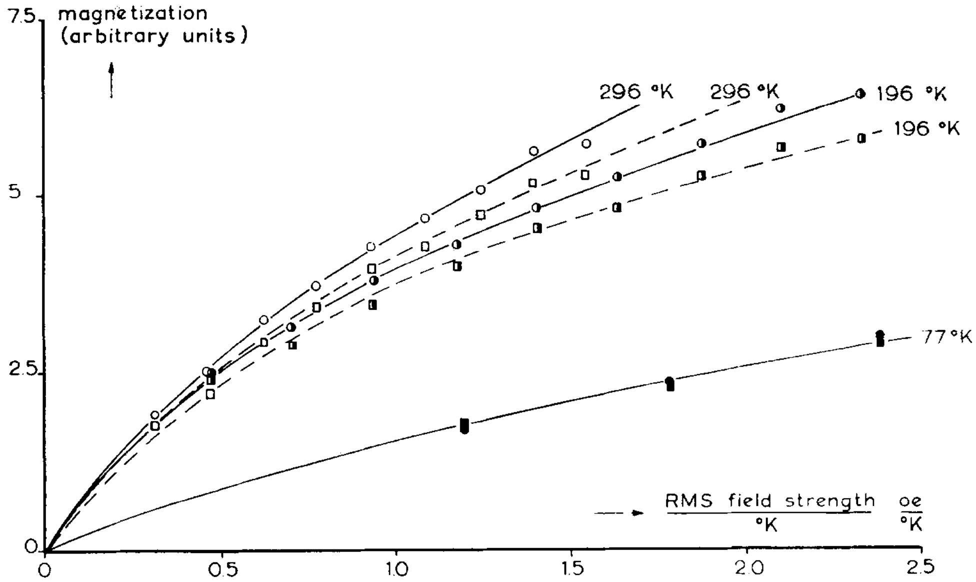


FIG. 8. Dependence of the magnetization of the nickel-on-kieselguhr catalyst on field strength and measuring temperature. Catalyst, 111½ hr reduced at 205°C. KEY: (☐) After 21 hr evacuation at 205°C; (○) after 109 hr evacuation at 205°C; (○ ☐) measured at 296°K; (◑ ◨) measured at 196°K; (● ■) measured at 77°K.

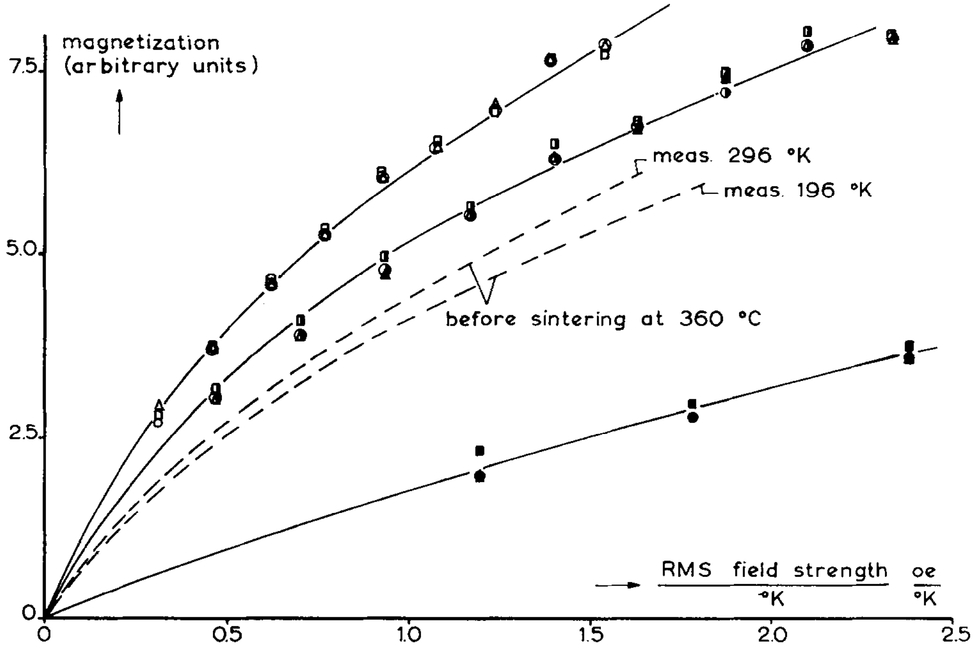


FIG. 9. Dependence of the magnetization of the nickel-on-kieselguhr catalyst on field strength and measuring temperature. Catalyst, 111½ hr reduced at 205°C. KEY: (☐) After 41 hr evacuation at 310°C; (△) after 45 hr extra evacuation at 210°C; (○) after 61½ hr extra evacuation at 210°C; (☐ △ ○) measured at 296°K; (◨ ▲ ◑) measured at 196°K; (■ ▲ ●) measured at 77°K.

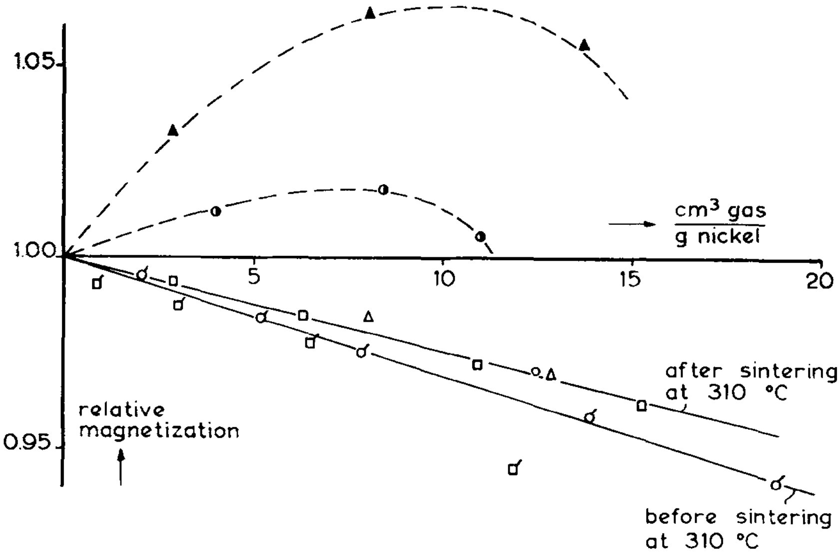


FIG. 10. Effect of hydrogen adsorption on the magnetization of the nickel-on-kieselguhr catalyst. Catalyst, 111½ hr reduced at 205°C. KEY: (□́ ○́) After evacuation at 205°C measured at 296°K; (□ △ ○) after evacuation at 310°C; (□ △ ○) measured at 296°K; (◑) measured at 196°K; (▲) measured at 77°K.

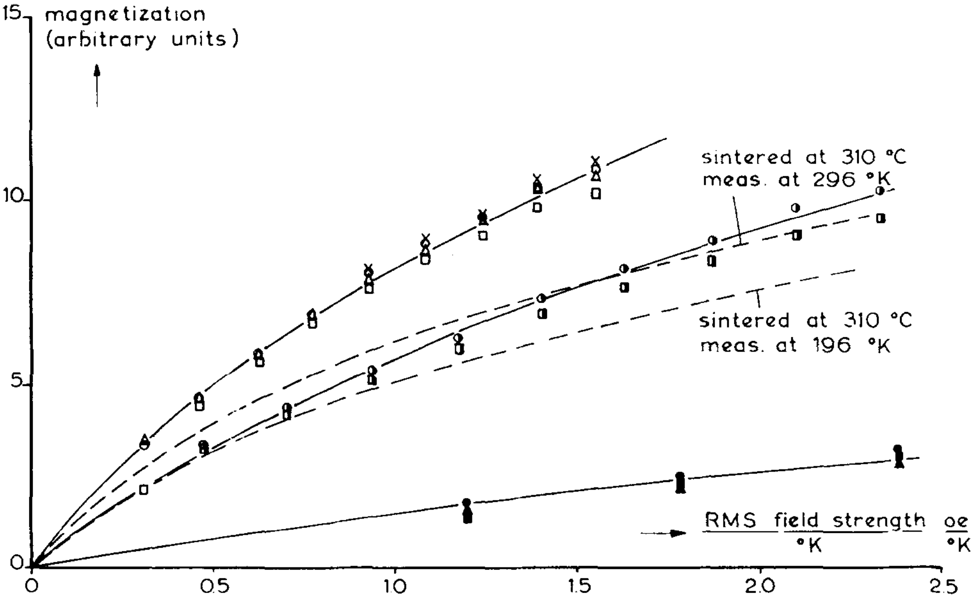


FIG. 11. Dependence of the magnetization of the nickel-on-kieselguhr catalyst on field strength and measuring temperature. Catalyst, reduced at 210°-250°C for 120 hr. KEY: (□) after 16½ hr evacuation at 490°C; (△) after 16 hr extra evacuation at 210°C; (○) after 32 hr extra evacuation at 210°C; (×) after 48 hr extra evacuation at 210°C; (□ △ ○) measured at 296°K; (◨ ◑) measured at 196°K; (■ ▲ ●) measured at 77°K.

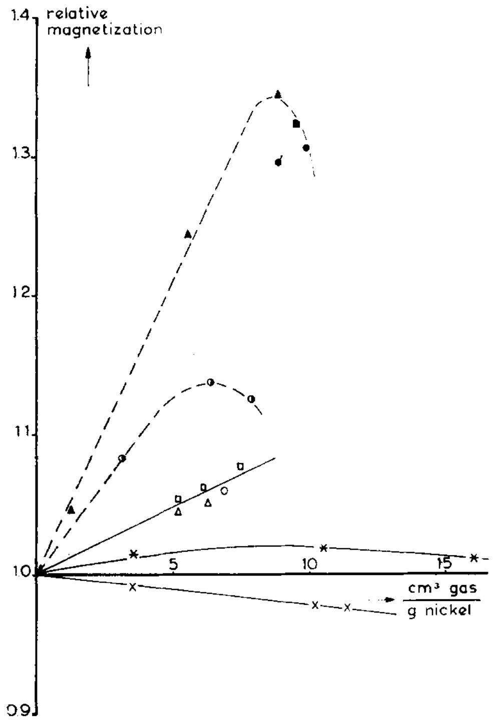


FIG. 12. Effect of oxygen and hydrogen adsorption on the magnetization of the nickel-on-kieselguhr catalyst. Catalyst reduced at 210°–250°C for 120 hr. KEY: (□) hydrogen adsorption after 16½ hr evacuation at 490°C, measured at 296°K, (■) measured at 77°K; (△) hydrogen adsorption after 16 hr extra evacuation at 210°C, measured at 296°K, (▲) measured at 77°K; (○) hydrogen adsorption after 32 hr extra evacuation at 210°C, measured at 296°K, (◑) measured at 196°K, (●) measured at 90°K, (●) measured at 77°K; (×) oxygen adsorption after 48 hr extra evacuation at 210°C, measured at 296°K, (∗) measured at 77°K.

urements essentially the same effects were observed.

DISCUSSION

(a) *Effect of Chemisorption on Superparamagnetic Particles*

As is seen from our experiments, the effect of hydrogen adsorption on the magnetization of superparamagnetic and nonsuperparamagnetic nickel particles is different. For superparamagnetic particles the decrease in magnetization does not depend on the measuring temperature; this was also observed by Dietz and Selwood (11) on particles that are superparamagnetic in the temperature range 77°–296°K.

For the coprecipitated nickel-on-silica catalyst reduced at 360°C the M versus H/T plot is linear up to an H/T value of about 1.5. From this it can be concluded that in the hydrogen adsorpton experiments on this catalyst, in which the magnetization was measured at 196° and 296°K in a field of 320 oe (Fig. 4), Eq. (3) is valid. Thus

$$M = (I_s^2H/3kT) \sum_i n_iv_i^2 \qquad (3)$$

or

$$M = (H/3kT) \sum_i n_in_{a_i}^2\mu_{\mathrm{Ni}}^2 \qquad (6)$$

where n_{a_i} is the number of atoms of the nickel particles with volume v_i and μ_{Ni} is the average magnetic moment of a nickel atom.

Tentatively assuming a system with uniform nickel particles with n_a atoms per particle, Eq. (6) changes into

$$M = (Hn_i/3kT)n_a^2\mu_{\mathrm{Ni}}^2 \qquad (7)$$

and

$$\tfrac{1}{2}dM/M = \frac{dn_a\mu_{\mathrm{Ni}}}{n_a\mu_{\mathrm{Ni}}} \qquad (8)$$

Assuming finally that the nickel particles are homogeneously covered with hydrogen and that N_{H} hydrogen atoms are adsorbed per nickel atom, the slope in the origin of the relative magnetization versus amount of absorbed hydrogen curve of the measurements at 196° and 296°K in Fig. 4 shows that

$$\frac{(dM/M)}{dN_{\mathrm{H}}} = 2.02 \qquad (9)$$

which leads to

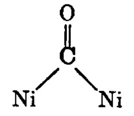
$$\frac{1}{n_a\mu_{\mathrm{Ni}}}\frac{dn_a\mu_{\mathrm{Ni}}}{dN_{\mathrm{H}}} = 1.01 \qquad (10)$$

In the Introduction mention was made of two mechanisms for the decrease in magnetization on chemisorption, viz., a covalent bonding of the electrons of the adsorbate with unpaired electrons of the *d*-

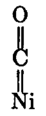
bond of the nickel, and the destruction of the ferromagnetic properties of a surface nickel atom by the attachment of an adsorbed atom or molecule.

In the first process, only the average magnetic moment per nickel atom changes ($dn_a = 0$), and from Eq. (10), since μ_{Ni} is 0.6, it follows that about 0.6 electron spin is paired per adsorbed hydrogen atom. (Judged from the experimentally determined g-value of 2.22, this number is slightly less.) In the second process $d\mu_{Ni} = 0$, and it appears from Eq. (10) that the adsorption of a hydrogen atom destroys the ferromagnetism of one nickel atom.

In view of the assumptions that had to be made in the derivation of Eq. (8), definite conclusions about the number of paired electron spins, or the number of nickel atoms made nonferromagnetic, per hydrogen atom cannot be drawn from these low-field measurements. A uniform particle size certainly does not exist in our system; as Dietz and Selwood (11) showed, a distribution of particle sizes could change the factor ½ before dM/M from 1/1.5 to 1/3.7. A homogeneous distribution of the admitted gases over the nickel particles is improbable since the first portion of the gas is irreversibly adsorbed on the metal at these temperatures. Starting from the outside of the catalyst grains, the nickel particles are covered one after another to some extent. Nevertheless it is interesting to note that, from measurements of the influence of hydrogen adsorption on the saturation magnetization of nickel, Dietz and Selwood (11) arrived at about the same number of spins paired per hydrogen atom. For our other superparamagnetic systems, Eq. (3) is not valid and the influence of hydrogen adsorption is less. From the experiments on superparamagnetic particles presented in Fig. 7, where the effects of hydrogen, oxygen, and carbon monoxide adsorption are compared, it follows that the over-all effect per adsorbed molecule is the same, indicating that the distribution of the admitted gases on the nickel particles is analogous and the number of d-electron spins paired per adsorbed molecule is equal. At higher coverages the influence of carbon monoxide gradually weakens. In many other experiments not mentioned here, this behavior was confirmed. For hydrogen and oxygen adsorption on nickel-on-silica catalysts, Schuit and van Reyen (4) reported the same behavior, whereas Leak and Selwood (22) observed a nearly identical trend for oxygen and hydrogen working with a nonsintered nickel-on-kieselguhr catalyst. As to oxygen, reaction of an oxygen atom with a surface nickel atom to form nickel oxide is probable, and in this process the ferromagnetic properties of one nickel atom per oxygen atom are destroyed. As the number of spins paired by hydrogen and oxygen is equal, this is in accordance with the value for the number of spins paired per hydrogen atom, obtained on the basis of the foregoing assumptions. The fact that the experiments point to equal spin-pairing effects per hydrogen and carbon monoxide molecule is not in contradiction with the usual opinion about the chemisorption bond of hydrogen and carbon monoxide. From infrared studies Eischens *et al.* (23) demonstrated the existence of two chemisorbed carbon monoxide species on nickel surfaces:



at low coverages



at high coverages

The curved character of the carbon monoxide plot indicates the gradual replacement of the two-site adsorption by a one-site adsorption.

(b) *The Effect of Chemisorption on Nonsuperparamagnetic Nickel Particles*

If nonsuperparamagnetic particles are present, the maximum in the curves clearly shows that there are two effects: an increase and, at the same time, a decrease in magnetization. Here the total effect strongly depends on the measuring temperature.

To explain the increase in magnetization, Dietz and Selwood (11) and Leak and Selwood (22) suggested the possibility of a decrease in anisotropy energy as a result of the adsorption of hydrogen. Our experiments prove this suggestion to be correct.

When the nickel particles appear to be superparamagnetic in our measurements (the frequency of the alternating field being 50 cycles/sec), they can at most reverse their magnetization in 1/50 sec.† When the system is nonsuperparamagnetic, some particles do not reverse their magnetization with the frequency of the measuring field, and they are not measured. Now, if the activation energy is decreased enough by the adsorption of hydrogen, particles whose magnetization cannot reverse in 1/50 sec. can, after adsorption, follow the measuring field and manifest themselves in the measurement. This increases the measured magnetization, whereas the magnetization of those particles which are already superparamagnetic is decreased by the adsorption. For the coprecipitated catalyst reduced at 360°C and measured at 77°K, the latter effect still exceeds the increase, but the total decrease is less than when only superparamagnetic particles are present. After reduction at 525°C, measurement at 77°K shows that the production of superparamagnetic particles by adsorption dominates. The nickel-on-kieselguhr catalyst contains larger Ni particles; here an increase was observed also on measuring at 196°K; at 77°K this effect is even more pronounced. After the catalyst was sintered at 460°C, the magnetization increased also at room temperature. The curves measured at 196° and 77°K show distinct maxima. This indicates that the decrease of the anisotropy energy and hence of the activation energy for rotation is limited.

Dietz and Selwood (11) raised some doubt as to the decrease-in-activation energy mechanism, because at 4.2°K they did not observe a decrease in remanence of a nickel-on-silica catalyst on hydrogen adsorption. To obtain a decrease in remanence, an appreciable lowering of the time needed for reversal of the magnetization is necessary, and such a lowering is not present. In our measurements, however, there is a sharp boundary (viz., 1/50 sec), and a small decrease in anisotropy energy can manifest itself.

The mechanism by which chemisorption lowers the magnetic anisotropy is difficult to explain. First, the problem of the origin of the magnetic anisotropy of the small nickel particles arises. This could be either the magnetocrystalline anisotropy or the presence of mechanical stress in the nickel particles. An effect of adsorption on the shape anisotropy is difficult to understand. If the magnetocrystalline anisotropy is operative only, the total anisotropy energy of a nickel particle is proportional to its number of nickel atoms. If for every hydrogen atom adsorbed one nickel atom is brought into a nonferromagnetic state by hydrogen adsorption, the total number of nickel atoms of a particle is decreased and hence also its anisotropy energy.

This simple explanation, however, is ruled out by the equal effects of hydrogen and oxygen adsorption on the magnetization of superparamagnetic particles and by the different effects on the anisotropy energy (see Figs. 7 and 12). For the magnetocrystalline anisotropy two basically different theories were put forward. The first ascribes the origin of the anisotropy to the modification of the spin coupling of neighboring atoms by the spin-orbit coupling of the initially quenched orbital states (24); the other points to the anisotropic electrostatic environment of the magnetic atoms (25). In spite of theoretical difficulties with regard to the latter theory, measurements by Bean *et al.* (26) on small cobalt particles in a copper matrix support the picture of the anisotropic electrostatic environment. They found that the magnetic anisotropy of ferromagnetic atoms

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† A strong influence of the measuring frequency was observed. A system with rather large nickel particles, superparamagnetic at 296°K when measured with 50 cycles/sec, was not superparamagnetic when measured with 1500 cycles/sec at the same temperature. As will be explained in the following, measurements at 50 cycles/sec showed a decrease on hydrogen adsorption, whereas at 1500 cycles/sec an increase was found. These investigations will be published later in full detail.

with the same electrostatic environment does not change. For the nickel atoms on the surface, which constitute a large fraction of the total amount of nickel atoms in the systems considered, the electrostatic environment is highly anisotropic; hence, also the anisotropy originating from these surface atoms is high. If now on hydrogen adsorption the surface nickel atoms remain in their crystallographic position and become nonferromagnetic, the contribution of the surface atoms is eliminated and the remaining nickel atoms having about the bulk electrostatic environment, do not change their contribution to the anisotropy energy. Thus the total anisotropy energy of the particles is substantially lowered by this process. If on oxygen adsorption the nickel surface atoms are displaced from their crystallographic positions in the nickel lattice, the environment of the subsurface nickel atoms is more anisotropic than before the adsorption. Their contribution to the total anisotropy of the particle is large, and the decrease in anisotropy of the particles is less than in the case of hydrogen adsorption. On the other hand, an anisotropic stress, if existing in the nickel particles, might determine the magnetoanisotropic behavior owing to the relatively large value of the magnetoelastic constants of nickel. When gases are adsorbed on the small particles, the contraction of the lattice by the surface energy is weakened and the inhomogeneous stress decreases.

For small sodium chloride crystallites, the contraction and its relief by adsorption was observed by Nicolson (27). Owing to the decrease in stress, the magnetic anisotropy decreases also. It should be possible to decide between the two theoretical explanations by means of measurements on small iron particles, since in this case the influence of stresses is weaker owing to the relatively smaller magnetoelastic constants.

Finally it appears from our results that comparison of the effects of adsorption of different gases on the low-field magnetization can be made on superparamagnetic nickel particles only, since, with nickel particles which are not superparamagnetic, the decrease in anisotropy energy differs from one gas to another.

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